MECHANISM FOR THE FORMATION OF SUGARS FROM FORMALDEHYDE, PART II

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ABSTRACT. The author's intent is to reaffirm through closer studies the mechanism for the formation of sugars from formaldehyde which he had proposed earlier, but which was disputed by a critic. The essence of the disagreement is the question of whether the expansion of the volume of the reaction mixture is the result of the thermal effect or is caused by the accumulation of an intermediate product. The author maintains that the latter possibility is indeed the case. He supports his argument with a description of his experimental apparatus, figures, and reaction systems. He reaffirms the validity of his procedures and of the dilatometric method for studying this reaction. He concludes that the thermal changes in the volume of the reaction mixture are insignificant. For this reason the kinetics of the reaction can be considered on the basis of volumetric change.

After the publication of my article [1] "Mechanism for the Formation of Sugars from Formaldehyde" an article was published by Kuzin [2], in which he, having earlier written about the mechanism of the formation of sugars from formaldehyde which he proposed, asserted that all of my judgments were based on an erroneous interpretation of the data which I had obtained. /2288*

The essence of my article consists in the following. Because of the fact that one molecule of sugar is formed from six molecules of formaldehyde as the result of the condensation of formaldehyde, the reaction which occurs in the liquid phase should be accompanied by a reduction in the volume. For the purposes of studying this reaction I designed an apparatus -- a dilatometer (Figure 1). It was established on the basis of studies that the volume decreases sharply at the beginning of the reaction and then begins to increase slowly, only to drop again after attaining a definite maximum. The curve depicting the changes in volume, which we have called a dilatometric curve, is illustrated in Figure 2.

The arm a - b of the curve (sharp reduction in volume), as I established experimentally, reflects the solubility of calcium oxide hydrate (lime); the arm b - c, the so-called induction period, is related to the accumulation of the intermediate product; c - d, specifically the condensation process, is the dissociation of the intermediate product with the formation of sugars, which can be represented schematically as follows:

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* Numbers in the margin indicate pagination in the foreign text.

$$A \rightleftarrows A'$$
$$A' + B \rightleftarrows F + 2H_2O$$
$$F + S \rightarrow FS_1' + H_2O$$
$$FS_1' + S \rightarrow FS_2' + H_2O$$
$$\cdots\cdots\cdots\cdots$$
$$\cdots\cdots\cdots\cdots$$
$$FS_6' \rightarrow 2B$$

where: A - calcium oxide hydrate in the solid state, A' - calcium oxide hydrate in solution, B - sugar molecule, F - saccharate molecule, S - hydrated formaldehyde molecule, $FS_1'FS_2'...FS_5'$ - embryonic centers or, in other words, molecules of the intermediate complex.

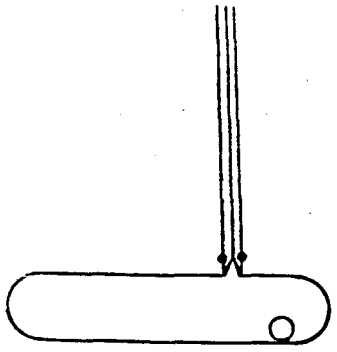

Fig. 1. Dilatometer

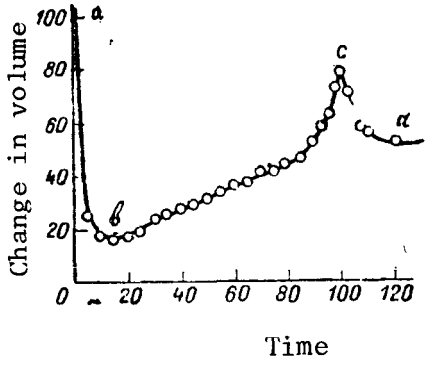

Fig. 2. Dilatometric Curve. Experimental Conditions: 20 grams of CaO, 10 ml of CH_2O, t 45°.

The processes: $A \rightleftarrows A'$ - the dissolving of lime - is accompanied by a reduction in volume; the formation of saccharates and the accumulation of the intermediate products - F, FS_1', FS_2', - are accompanied by the liberation of three water molecules and an increase in volume, whereupon this process continues as long as formaldehyde molecules exist, and then the intermediate complex FS_6 begins to dissociate with the formation of sugar and lime, some of which precipitates, and then the volume begins to decrease again (arm c - d of the dilatometric curve). /2289

A.A. Kuzin, considering that the process takes place as the result of the formation of endiol sugars in an alkaline medium, which catalyze the condensation of formaldehyde, intimated that the second arm of the dilatometric curve which I obtained is only the result of the thermal expansion of the liquid (the reaction mixture), since the condensation of formaldehyde is accompanied by the liberation of heat and that the entire system of the mechanism which I proposed for the condensation of formaldehyde into sugars is erroneous, since it is an inaccurate consideration of the experimental data.

After carefully carrying out numerous tests on solutions of formaldehyde and sugar additives, used as catalysts, with varying ratios of lime, I established the following:

1. Formaldehyde condenses in the presence of the hydrates of the oxides of the alkaline earth metals, including lime. The addition of monosacharides significantly accelerates the reaction of formaldehyde condensation, but only in the presence of lime or of other hydrates of alkaline earth metal oxides.

2. During condensation the solubility of lime increases, but then diminishes somewhat, whereupon some of it precipitates (Figure 3). The solubility curve of lime is in agreement with the dilatometric curve. This indicates that lime takes part not only in the creation of the definite alkalinity of the medium, which provides for the formation of the endiol sugars, as acknowledged by Kuzin, but that lime, as follows from our system, also enters into the intermediate complex (embryonic centers) as a component part. /2290

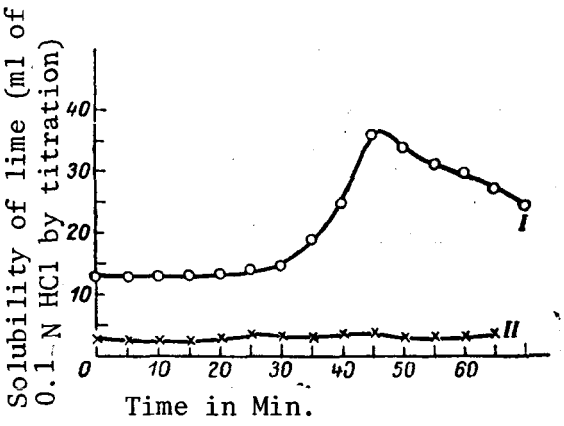

Fig. 3. Solubility of Lime During the Condensation Reactions of Formaldehyde. Key: I - 6 g CaO, 30 ml CH_2O, 0.2 g Glucose, t 40°; II - After Treating the Solution with CO_2 in the Experiment Represented by Curve 1.

3. The condensation of formaldehyde in the presence of lime is actually accompanied, as Kuzin noted, by the liberation of heat. In our experiments the increase in the temperature varied within the limits of 0.9 to 1.40°, depending on the ratio of the quantities of lime and formaldehyde, whereupon the maximum increase in temperature practically coincided with the peak of the dilatometric curve.

By knowing the temperature coefficient of the expansion of water (solvent), the volume of the vessel, diameter of the capillary, which is used to measure the changes in the volume of the liquid, it is easy to calculate the change in its volume resulting from the thermal effect.

My data are shown in the table.

These data, represented graphically in Figure 4, show at a glance that the expansion of the volume as a result of the thermal effect is relatively small. The assertion of Kuzin that the change in volume is only the result of the thermal expansion of the liquid is not correct, and his conclusion, which is critical of all of our work, is completely without foundation.

The large amounts of experimental work which I conducted after the publication of Kuzin's article enables me to submit with complete justification

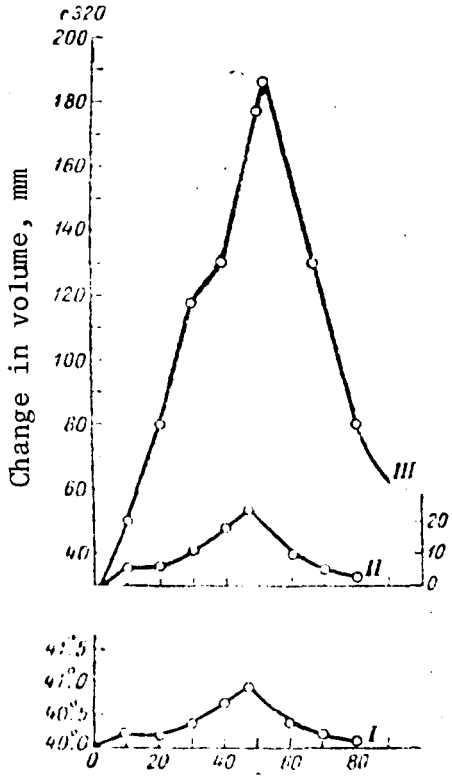

Fig. 4. Changes in Temperature and Volume as a Function of the Thermal Effect of the Reaction and as a Result of Condensation. Experimental Conditions: 3 g $Ca(OH)_2$, 30 ml of 40% CH_2O Solution, 0.2 g of Glucose. Key: I - Changes in Temperature; II - Changes in Volume as a Result of the Thermal Effect; III - Dilatometric Curve.

that this critique is not valid and to have the satisfaction once again of being convinced in the validity of the condensation mechanism of formaldehyde into sugars in the presence of the hydrates of the alkaline earth metal oxides which I have propounded. /2291

I wish to take this opportunity to express my deepest gratitude to Professor Kuzin for his review of my work, since his criticism prompted me to undertake a large amount of experimental work which not only completely confirmed my first proposal of the mechanism of the condensation of formaldehyde, but which produced new material which served as the basis for the creation of the monograph for this problem [3].

Conclusions

1. The method proposed by the author for the study of the kinetics of the condensation of formaldehyde to sugars was re-examined.

2. That the dilatometric method of investigating this reaction is completely valid for the study of kinetics has been proved.

3. It has been shown that the thermal changes in the volume of the reaction mixture have no effect on the overall process of the change in volume and, consequently, make it possible to judge the kinetics of the reaction on the basis of its change.

No. of tests	Ratio of CH_2O in ml to $Ca(OH)_2$	Increase in Temperature resulting from reaction (in degrees)	Increase in Volume resulting from thermal effect (in mm through capillary)	Changes in volume by dilatometric curve (in mm through capillary)
8	20/3	0.95	25	125
9	30/4	1.1	29	125
10	30/3	1.0	26.5	150
11	35/5	1.4	37	151

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